Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.941301

56 (2015) 684–694
October

Taylor & Francis
Taylor & Francis Group

Investigation of organic matter adsorption from TNT red water by modified bamboo charcoal

Dan Fu[a,b], Yihe Zhang[a,c,*], Xianghai Meng[a], Fengzhu Lv[a,*], Paul K. Chu[c], Kun Tong[a]

[a]*National Laboratory of Mineral Materials, School of Materials Sciences and Technology, China University of Geosciences (Beijing), Beijing 100083, China, Tel. +86 416 3212088; email: fudan20030333@126.com (D. Fu), Tel. +86 10 82323433; emails: zyh@cugb.edu.cn (Y. Zhang), mengxianghai_2006@163.com (X. Meng), lfz619@cugb.edu.cn (F. Lv), Tel. +86 13904279390; email: jiankang8848@sina.com (K. Tong)*

[b]*Department of Chemistry, Liao Ning Petrolchemical Vocational and Technology College, Liaoning 121001, China*

[c]*Department of Physics & Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China, Tel. +852 34427724; email: paul.chu@cityu.edu.hk (P.K. Chu)*

Received 14 November 2013; Accepted 26 June 2014

ABSTRACT

Bamboo charcoal impregnated with $ZnCl_2$ ($ZnCl_2$-BC) was used as an adsorbent to remove organic matters from TNT red water. The adsorption parameters, such as the adsorbent dosage, pH, contact time, dilution ratios of TNT red water, and temperature were studied. The equilibrium adsorption data were analyzed using Langmuir, Freundlich, and Temkin isotherms models. The Langmuir isotherm fitted the experimental results well. Kinetic analyses results showed that the adsorption kinetics was more accurately represented by the pseudo-second-order model. The studies of external diffusion and intraparticle diffusion models showed that external as well as intraparticle diffusions influenced on the actual adsorption process at different times and the removing velocity of organic matters from solution to the surface of adsorbent was very rapid. Thermodynamic studies showed that the adsorption of organic matters from TNT red water on $ZnCl_2$-BC was a spontaneous, endothermic, and random process at the solid/solution interface. The Dubinin–Radushkevich (D–R) models, thermodynamics, and the activation energy analysis indicated the adsorption was a physical mechanism. The adsorption was enforced by van der Waals force, hydrogen bonding formation electron, donor–acceptor interaction, and base and acid interaction based on HSAB theory.

Keywords: Adsorption; $ZnCl_2$-Bamboo Charcoal; Organic matter; TNT red water

1. Introduction

2,4,6-Trinitritoluene (TNT) is a widely used nitroaromatic explosive since 1900s [1]. During manufacturing and refining of TNT, a large amount of TNT red water is produced. The TNT red water has a dark red color and complex compositions. According to the previous reports, α-TNT and dinitrotoluene sulfonates, 2,4-DNT-3-SO_3^- and 2,4-DNT-5-SO_3^- are the main organic components in TNT red water [2,3]. The red water, if untreated, results in serious environmental problems by contamination of soil and underground water, further affects the health of human since TNT red water is toxic, carcinogenic, mutagenic, and not easily biodegraded [4].

*Corresponding authors.

Many methods have been developed to remove organic matters from the TNT red water, namely adsorption [3,5], wet air oxidation [6,7], and vacuum distillation [8]. Among which adsorption is still one of the most extensively used and effective methods for organic matters removal from TNT red water, but the wide applications of absorbents are limited by the high cost. Many researches have focused on developing more efficient and economical adsorbents to treat TNT red water.

Bamboo with short growth cycle is abundant, especially in China. So it can be used as renewable and low-price biomass resource. A large number of bamboo solid wastes can be produced from factory of bamboo manufacturing a year. Accumulation of bamboo solid wastes is a big menace to the environment. Bamboo charcoal (BC) from bamboo solid wastes has been used as a low-cost adsorbent to treat various organic pollutants [9–11].

We had reported on the adsorption of TNT red water using BC [12]. Although BC can treat TNT red water, the adsorption efficiency was low. According to the base and acid theory by Pearson [13] and our study on the adsorption of organic matters from TNT red water by Cu^{2+} impregnated activated carbon [14], it is preferred $ZnCl_2$-modified BC ($ZnCl_2$-BC) would possess high removal efficiency, so the adsorption of organic matters from TNT red by water $ZnCl_2$-BC was studied in detail. The effects of adsorbent amount, pH, contact time, dilution ratios of red water, and temperature on adsorption characteristics as well as the adsorption kinetics, equilibrium isotherms, and mechanism are studied in detail.

2. Materials and methods

2.1. Adsorbent

2.1.1. Preparation of $ZnCl_2$-BC

BC supplied by Chinese Academy of Forestry, Beijing, China was washed with distilled water to remove impurities, oven dried at 105°C, and then used to prepare $ZnCl_2$-BC. The BC was dipped into 3 mol/L of $ZnCl_2$ solution and kept at 70°C for 12 h. The modified BC was filtered, dried, and then carbonized at 800°C for 1 h. The carbonized BC was repeatedly washed with water to remove the excess of $ZnCl_2$ until Cl^- could not been tested out by silver nitrate. The prepared $ZnCl_2$-BC was kept in vacuum desiccators for further use.

2.1.2. Characterization of the $ZnCl_2$-BC

The surface area, pore volume, and average pore diameter of $ZnCl_2$-BC were measured by N_2 adsorption isotherm using an ASAP 2020 Micromeritics instrument.

The functional groups on the surface of $ZnCl_2$-BC were investigated by Boehm's titration. The point of zero charge (pH_{PZC}), which is the pH value required to give zero net surface charge, was determined by a mass titration method proposed by Noh and Schwarz [15]. The pH was measured by a pH meter (pHSJ-4A, Shanghai, China).

A scanning electron microscope (SEM, HITACHI S-450 at 10 kV) was employed to examine the surface morphology of $ZnCl_2$-BC before and after adsorption of TNT red water. X-ray diffraction (XRD) patterns were acquired on a Rigaku. D/max-rA (12 kW and Cu K_α radiation).

2.2. Adsorbate

2.2.1. TNT red water solution

The TNT red water provided by the 525 ammunition plant (Hubei Province, China) was reddish brown with high COD. The physical and chemical properties of TNT red water were given in our previous research [12]. Different concentrations of TNT solutions were prepared by further dilution. The pH of TNT red water was adjusted by 0.1 mol/L NaOH and 0.1 mol/L HCl solutions.

2.2.2. Chemical oxygen demand (COD) analysis of TNT red water

According to the report, the CODs of TNT red water before and after adsorption were determined by a colorimetric method [12].

The COD adsorption at equilibrium, q_e (mg/g), and COD removal (%) were calculated as follows:

$$q_e = \frac{(c_0 - c_e)V}{W} \quad (1)$$

$$\text{Removal of COD } (\%) = \frac{(c_0 - c_e)}{c_0} \times 100 \quad (2)$$

where c_0 and c_e (mg/L) are the initial and equilibrium TNT red water COD, respectively. $V(L)$ is the volume of TNT red water and W (g) is the adsorbent weight. At any time, the amount of COD adsorbed (mg/g) (q_t) by the $ZnCl_2$-BC can be calculated by Equation (1) and the notations were accordingly adapted.

2.3. Adsorption experiments

Batch adsorption experiments were conducted using $ZnCl_2$-BCs as the adsorbents in 250 mL of

flasks containing 25 mL of TNT red water. The flasks were agitated at 150 rpm in a temperature-controlled shaker (ZD-85, Changzhou, China) to reach equilibrium. The adsorbent dosage, pH value, and contact time for the adsorption efficiency study were in the range of 0.1–0.9 g/25 mL, 2.0–12.0, and 10–480 min for 100 times diluted TNT red water at 30 ± 0.2℃, respectively. The effect of dilution ratios of TNT red water was studied for 1:50–1:150 times of TNT red water at 30 ± 0.2℃. The adsorption isotherms, thermodynamics, and kinetics were studied using 100 times diluted TNT red water at an adsorbent dosage of 0.3 g/25 mL at 30, 40, 50, and 60 ± 0.2℃.

3. Results and discussion

3.1. Characterizations of $ZnCl_2$-BC

Table 1 shows the characterizations of the $ZnCl_2$-BC. The specific surface area and pore volume of $ZnCl_2$-BC have obviously increased compared with the BC (data shown in Ref. [12]). The results of Boehm's titration reveal the presence of surface functional groups of carboxylic, phenolic, lactones, and basic groups on the ZnCl2-BC, and the main functional groups are acid groups [16,17].

The surface morphology and structure of $ZnCl_2$-BC are determined by SEM and XRD. The SEM images of BC and $ZnCl_2$-BC (Fig. 1) show that the $ZnCl_2$-BC still has a porous and coarse surface as BC. The XRD spectrum of $ZnCl_2$-BC in Fig. 2 shows a broad peak around 23° which comes from the amorphous structure of BC. There are no crystalline peaks in the XRD pattern of $ZnCl_2$-BC showing the structure of $ZnCl_2$-BC is also amorphous.

Table 1
The results of Boehm's titration, pH, pZC, and the N_2 adsorption isotherm of $ZnCl_2$-BC

Parameter	The value
Carboxylic groups	0.1023 mmol/g
Phenolic groups	0.1332 mmol/g
Lactonic groups	0.0990 mmol/g
Acid groups	0.3345 mmol/g
Basic groups	0.1255 mmol/g
pH_{PZC}	7.52
BET	549.78 m^2/g
Pore volume	0.3356 cm^3/g
Average pore diameter	2.44 nm

3.2. Effect of adsorbent dosage on adsorption of organic matters in TNT red water

Fig. 3 shows the influence of adsorbent dosages on the adsorption of organic matter by the $ZnCl_2$-BC. The removal of COD (%) increases rapidly with adsorbent dosage up to 0.5 g and then slows down. The increased removals of COD (%) are due to the increasing number of active sites and the more available surface since large dosage of absorbents is used. Fig. 3 shows only when the dosage of $ZnCl_2$-BC was higher than 0.5 g, the removal of COD did not change obviously. But in application, large amount of $ZnCl_2$-BC indicates high cost. Considering these two factors, the crosspoint of the slope of the first-part line and the second part is determined as the optimal dosage (0.3 g).

3.3. Effect of pH on the adsorption of organic matters in TNT red water

Fig. 4 shows the effect of pH value on the adsorption of organic matters from TNT red water by $ZnCl_2$-BC. The optimum pH value is determined at 2.0, at which the removal degree of COD is 93.6%. The main components of TNT red water are dinitrotoluene sulfonate (Ph-SO_3M) and α-TNT. Some α-nitrophenols (NBCs-OH), α-nitrobenzoic acid (NBCs-COOH), and other nitrobenzene compounds (NBCs) are also presented in TNT red water [14]. In the aqueous solution, the dinitrotoluene sulfonates are dissociated and converted to anionic forms [18]:

$$Ph-SO_3M \xrightarrow{H_2O} Ph-SO_3^- + M^+ \quad (3)$$

And in an acid medium, most of the organic matters in TNT red water exist in the molecular form because of difficulty to ionize. In a basic medium, α-TNT forms the Janovsky complexes [12,19]. And the solubility of α-TNT is low [20]. In addition, the α-nitrophenols and α-nitrobenzoic acid in TNT red water easily ionize to various anionic forms [21], as shown in Eqs. (4) and (5):

$$NBCs-OH \xrightarrow{OH^-} NBCs-O^- + H_2O \quad (4)$$

$$NBCs-COOH \xrightarrow{OH^-} NBCs-COO^- + H_2O \quad (5)$$

Therefore, at $pH < pH_{PZC}$ of $ZnCl_2$-BC ($pH_{PZC} = 7.52$ for $ZnCl_2$-BC), the total surface charge of $ZnCl_2$-BC is

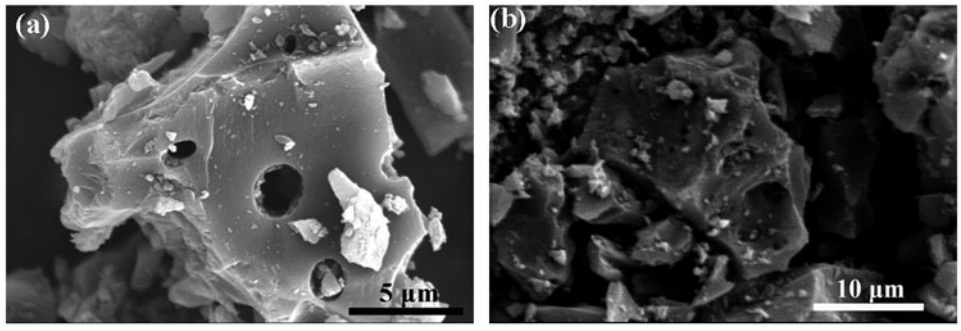

Fig. 1. SEM micrographs of BC and $ZnCl_2$-BC.

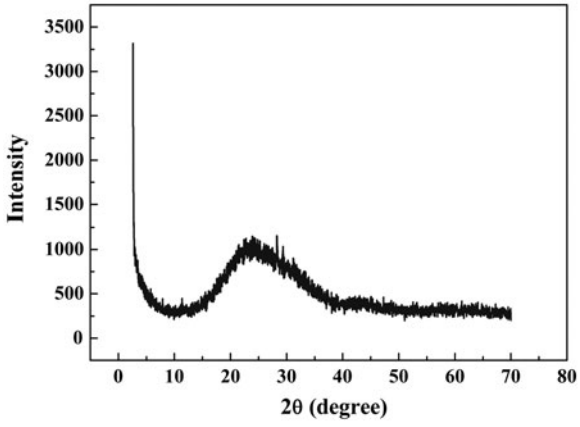

Fig. 2. XRD pattern of $ZnCl_2$-BC.

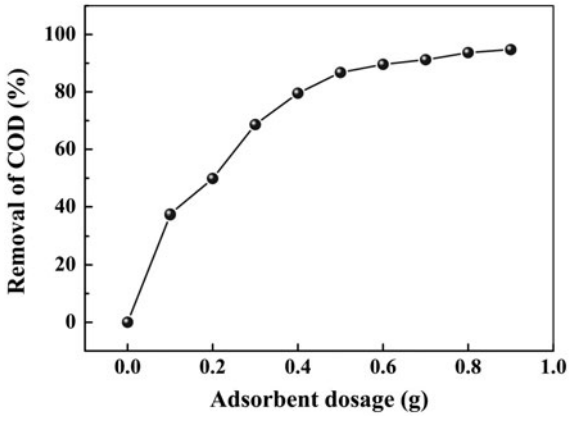

Fig. 3. Effect of adsorbent dosage on the adsorption of organic matters (temperature = 30 ± 0.2°C, V = 25 mL, ratio of dilution = 1:100, contact time = 180 min).

positive leading to the increase removal of COD due to the electrostatic force of attraction. Furthermore, the non-polar adsorbent, $ZnCl_2$-BC, tends to adsorb organic matters in molecular form. The lower the pH

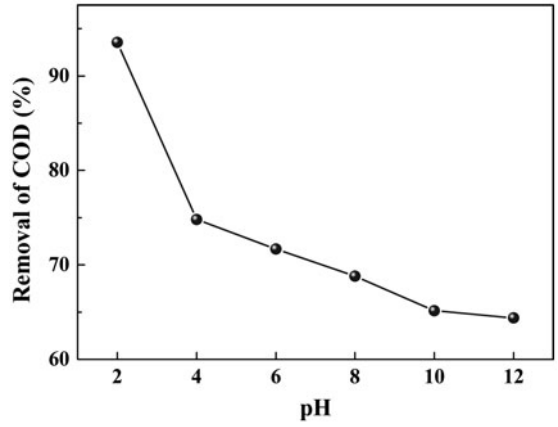

Fig. 4. Effect of pH on the adsorption of organic matters (temperature = 30 ± 0.2°C, adsorbent dosage = 0.3 g/25 mL, ratio of dilution = 1:100, contact time = 180 min).

of the solution is, the more organic molecules are adsorbed. Hence, the removal degree of COD reaches maximum at pH 2.0. However, at pH > pH_{PZC}, the $ZnCl_2$-BC surface has negative charge and lots of anions exist in TNT red water. Thus, the removal degree of COD is small because of electrostatic repulsion. Also the Janovsky of complexes and the low solubility of α-TNT bring negative effects on the adsorption [12].

3.4. Effect of contact time on the adsorption of organic matters of TNT red water

Fig. 5 shows the influence of contact time on adsorption of organic matters. The removal degree of COD is extremely fast in the first 30 min and then levels off after equilibrium. A large number of vacant surface sites are available for adsorption during the initial stage, but it is harder to occupy the remaining vacant surface sites due to the repulsive force between the adsorbed molecules on the solid and that in

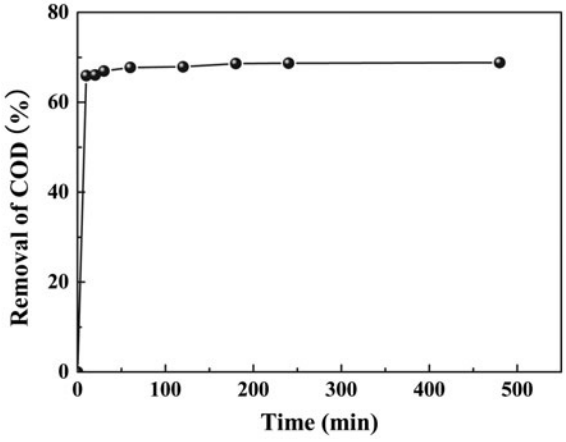

Fig. 5. Effect of contact time on the adsorption of organic matters (temperature = 30 ± 0.2℃, adsorbent dosage = 0.3 g/25 mL, and ratio of dilution = 1:100).

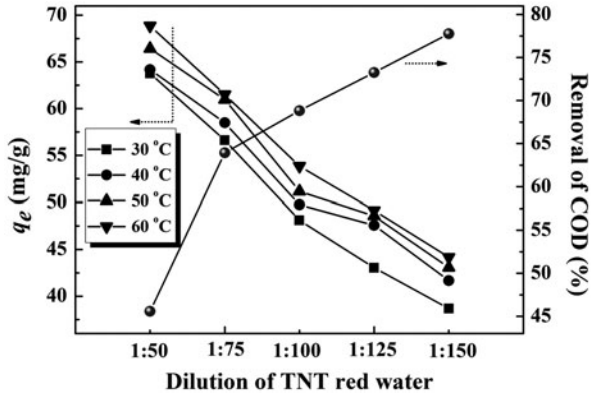

Fig. 6. Effect of dilution ratios of red water and temperature on the adsorption of organic matters (adsorbent dosage = 0.3 g/25 mL, contact time = 180 min).

solution equilibrium. Therefore, the contact time is determined as 180 min after equilibrium is reached. Similar contact time was reported on adsorption of organic matters from TNT red water using active coke and BC [4,12].

3.5. Effect of dilution ratios on adsorption of organic matters of TNT red water

Fig. 6 shows that the removal of COD (%) increases from 45.58% to 77.76% as the dilution ratio of TNT red water increases from 1:50 to 1:150. The adsorbed organic matters in per unit volume of TNT red water decrease with the increasing of dilution ratios. However, an increase in the dilution ratios of TNT red water reduces the diffusion of organic molecules from solution to the adsorbent surface due to the decrease in driving force of concentration gradient. Hence, the amount of adsorbed COD at equilibrium decreases from 63.77 to 38.68 mg/L as the dilution ratio is increased from 1:50 to 1:150.

3.6. Effect of temperature on adsorption of organic matters of TNT red water

The effect of temperature on the adsorption capacity of organic matters is studied at four different temperatures (30, 40, 50, and 60 ± 0.2℃) using 100 times diluted TNT red water and the results are shown in Fig. 6. The adsorption capacity increases slightly from 48.11 to 53.85 mg/g as the temperature increases from 30 to 60℃ indicating that the adsorption process is controlled by diffusion (intraparticle transport-pore diffusion) and the adsorption process is endothermic [22]. This may be because the mobility of organic matters in the TNT red water increases and the resistance on the diffusing particles decreases at a higher temperature which consequently boosts the adsorption capacity. In addition, the higher mobility of molecules facilitates the formation of a surface monolayer at higher temperature [23].

3.7. Adsorption isotherms

The purpose of analyzing the adsorption isotherms is to reveal the specific relationship between the equilibrium concentration of adsorbate and the adsorbed amount of organic matters on the surface of adsorbent. The Langmuir, Freundlich, Temkin, and D–R isotherm models were used in this paper. The Langmuir [24] isotherm equation can be written as follows:

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m} \tag{6}$$

where q_e (mg/g) is the amount of COD adsorbed by per unit mass of $ZnCl_2$-BC at equilibrium, c_e (mg/L) is the red water COD at equilibrium, q_m (mg/g) is the amount of maximum COD adsorbed by per unit mass of $ZnCl_2$-BC, and b (L/mg) is the Langmuir adsorption constant. The values of q_m and b (Table 2) can be calculated from the slope and the intercept of the plot of c_e/q_e vs. c_e.

The correlation coefficient values shown in Table 2 are satisfactory ($R^2 > 0.99$) for all experimental temperatures, indicating that the Langmuir isotherm fitted the experimental results well.

To determine whether an adsorption system is favorable or unfavorable, the separation factor (R_L) is defined based on the following equation [25]:

Table 2
Parameters of Langmuir, Freundlich, Temkin, and D–R isotherm models for organic matter adsorption on $ZnCl_2$-BC from TNT red water

Isotherm	Parameters			
Temperature (℃)	30	40	50	60
Langmuir				
q_m (mg/g)	69.03	70.02	71.07	74.46
b (L/mg)	0.0081	0.0136	0.0165	0.0166
R^2	0.9989	0.9984	0.9987	0.9988
Freundlich				
K_f (mg/g(L/mg)$^{1/n}$)	10.55	17.69	19.54	20.34
n	3.69	5.14	5.39	5.37
R^2	0.9563	0.9488	0.9497	0.9906
Temkin				
K_T (L/g)	0.13	0.64	0.93	0.98
B	13.74	10.33	10.12	10.48
R^2	0.9717	0.9608	0.9581	0.9945
Dubinin–Radushkevich				
q_m (mg/g)	58.73	59.90	60.83	61.54
B (mol^2/kJ^2)	1204.01	515.00	345.25	236.75
E (kJ/mol)	0.0204	0.0312	0.0381	0.0460
R^2	0.8846	0.8564	0.8108	0.7289

Notes: Adsorbent dosage = 0.3 g/25 mL; Dilution ratio = 1:50–1:150; Temperature = 30–60 ± 0.2℃ and Contact time= 480 min.

$$R_L = \frac{1}{1 + bc_0} \tag{7}$$

where b (L/mg) is the Langmuir constant and c_0 (mg/L) is the COD of initial TNT red water. There are four probable situations for R_L values. For favorable adsorption, $0 < R_L < 1$ and for unfavorable adsorption, $R_L > 1$, whereas for linear sorption, $R_L = 1$ and for irreversible sorption, $R_L = 0$ [26,27]. Fig. 7 shows the variations of the R_L with initial TNT red water dilution ratio. The R_L values for adsorption of organic matters are between 0 and 1 in the studied temperature, so the adsorption of organic matters by $ZnCl_2$-BC is a favorable process.

The linear form of the Freundlich [28] isotherm equation is:

$$\log q_e = \log K_f + \frac{1}{n}\log c_e \tag{8}$$

where q_e is the amount of COD adsorbed per unit mass of $ZnCl_2$-BC at equilibrium (mg/g), c_e (mg/L) is the equilibrium TNT red water COD, and K_f (mg/g (L/mg)$^{1/n}$) and n are Freundlich constant and intensity factors, respectively. The parameters were given in Table 2.

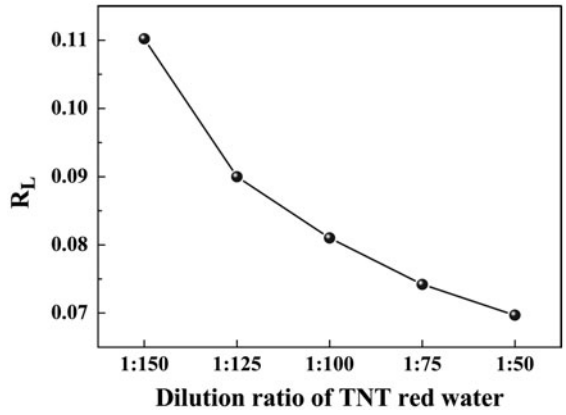

Fig. 7. Variation of separation factor (R_L) with the dilution ratios of TNT red water.

The correlation coefficient values ($R^2 = 0.9563$, 0.9488, 0.9497, 0.9906) from Freundlich model are summarized in Table 2 and less satisfactory compared with that of Langmuir model. But the constant $2 < n < 10$ still indicates that adsorption is favorable.

The Temkin [29] isotherm model can be linearized as:

$$q_e = B \ln K_T + B \ln c_e \tag{9}$$

where $RT/b = B$, b and K_T are constants, K_T is the equilibrium binding constant corresponding to the maximum binding energy, and constant B is related to the heat of adsorption. A plot of q_e vs. lnc_e enables the determination of the isotherm constant K_T and B.

The Temkin isotherm values, B and K_T, (Table 2) indicate that the heat for adsorption of all the molecules decreases linearly with coverage due to the adsorbent–adsorbate interactions and that adsorption is characterized by a uniform distribution of the binding energies [30].

The D–R isotherm [31] capable of distinguishing physical and chemical adsorption is more general because it does not assume a homogenous surface. The linear form of the D–R equation is given as:

$$\ln q_e = \ln q_m - B\varepsilon^2 \tag{10}$$

$$\varepsilon = \mathrm{RT} \ln\left(1 + \frac{1}{c_e}\right) \tag{11}$$

where q_m is the adsorption capacity (mol/g), B is a constant related to the adsorption energy (mol^2/kJ^2),

and ε is the polanyi potential, R is the gas constant (8.314 J/mol K), and T is the absolute temperature. The constant B gives the free energy E (kJ/mol) of the transfer of 1 mol of solute from infinity to the surface of adsorbent and can compute using the relationship:

$$E = \frac{1}{\sqrt{-2B}} \tag{12}$$

A plot of $\ln q_e$ vs. ε^2 gave straight lines. The values of q_m (mol/g) and B (mol^2/kJ^2) were obtained from the intercept and slope of the straight line.

The E value from D–R isotherm is useful for estimating the type of adsorption. If this value is less than 8 kJ/mol, the adsorption type can be physical adsorption. Otherwise, the adsorption type can be chemical adsorption [31,32]. The E values (Table 2) less than 8 kJ/mol in the present work suggest that adsorption process is a physical adsorption mechanism.

3.8. Adsorption thermodynamics

The adsorption amount of COD to 100 times diluted TNT red water by $ZnCl_2$-BC after equilibrium at 30, 40, 50, and 60 ± 0.2 °C is used to calculate the thermodynamics parameters including free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) according to the following equations [12,33,34]:

$$K_C = \frac{c_0 - c_e}{c_e} \times \frac{\rho V}{m} = \frac{q_e \rho}{c_e} \tag{13}$$

$$\Delta G = -\mathrm{RT} \ln K_C \tag{14}$$

$$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{15}$$

where K_C is the distribution coefficient, $\rho = lg/L$ is the density of the solution mixture, c_0 (mg/L) is the COD of initial TNT red water, c_e (mg/L) is the TNT red water COD after equilibrium, q_e is the COD amount of adsorption after equilibrium (mg/g), T is the solution temperature (K), and R is the gas constant (8.314 J/mol K). ΔH and ΔS are calculated from the slope and intercept of the linear plot of $1/T$ vs. $\ln K_C$ (figure not shown here). The values of K_C, ΔG, ΔH, and ΔS are summarized in Table 3. The free energy changes, ΔG, are negative under the experimental conditions indicating that adsorption of organic matters from the TNT red water is spontaneous. The positive values of ΔH indicate that the adsorption of organic matters on the $ZnCl_2$-BC is an endothermic process. In addition, the value of ΔH (11.49 kJ/mol) is between 2 and 40 kJ/mol indicating a physical adsorption characteristic [35]. The entropy change ΔS is positive indicating that the randomness increases during adsorption [36].

3.9. Adsorption kinetics

3.9.1. Frusawa and Smith (F&S) model

The external mass transfer coefficients for the organic matter adsorption were determined using a diffusion model referred as the F&S model [29]:

$$\ln\left(\frac{c_t}{c_0} - \frac{1}{1+mK_L}\right) = \ln\frac{mK_L}{1+mK_L} - \frac{1+mK_L}{mK_L}\beta_L S_S t \tag{16}$$

where c_t is the concentration after time t (mg/L), c_0 is the initial adsorbate concentration (mg/L), m is the mass of adsorbent per unit volume of free particle adsorbate (g/L), K_L and β_L are the Langmuir constant (obtained by multiplying q_m and b) (L/mg) and the mass transfer coefficient (cm/s), respectively. S_S is the outer surface area of adsorbent per unit volume of particle free slurry (1/cm). In general, the value of S_S is difficult to determine. Then, the $\beta_L S_S$ value was used to describe the adsorption process [37,38].

The plots of $\ln(c_t/c_o - (1/1+mK_L)$ vs. t for adsorption of organic matters at various temperatures are shown in Fig. 8. The value $\beta_L S_S$ was calculated from the slope of the straight line in Fig. 8 and was found to be as $1.58 \times 10^{-4}\,s^{-1}$, $1.85 \times 10^{-4}\,s^{-1}$, $1.74 \times 10^{-4}\,s^{-1}$, and $1.78 \times 10^{-4}\,s^{-1}$ for organic matters at different temperatures. This value indicates that the velocity of organic matters transporting from liquid phase onto the surface of $ZnCl_2$-BC is rapid enough for the removal of organic matters from TNT red water by $ZnCl_2$-BC. The same conclusion was obtained by Dan FU, Özer et al. and Panday et al. [12,18,37].

3.9.2. Pseudo-second-order model

Pseudo-second-order model was used to analyze the adsorption kinetics of $ZnCl_2$-BC to organic matters from TNT red water. The pseudo-second-order equation is expressed as [39]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{17}$$

where k_2 (g/mg min) is the pseudo-second-order constant, q_t (mg/g) is the amount of adsorbate at time t, q_e and k_2 can be determined experimentally from the

Table 3
Thermodynamic parameters for adsorption of organic matters from TNT red water on $ZnCl_2$-BC

Temperature (°C)	K_C (mg/L)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol·K)
30	183.8505	−13.13	11.49	81.41
40	222.3668	−14.06		
50	248.2453	−14.81		
60	279.399	−15.59		

Notes: Adsorbent dosage = 0.3 g/25 mL; Dilution ratio = 1:100; Temperature = 30 – 60 ± 0.2℃ and Contact time = 480 min).

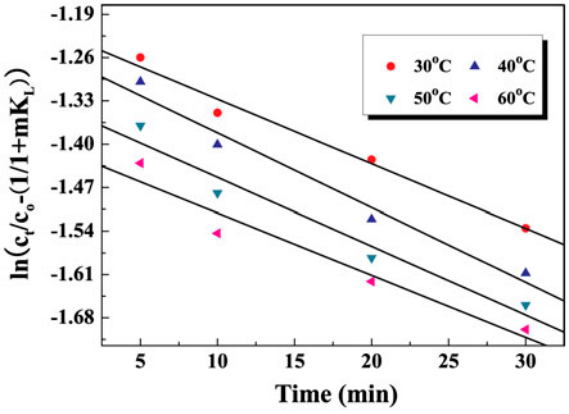

Fig. 8. Mass transfer plot for the adsorption of organic matters on $ZnCl_2$-BC.

slope and intercept of the plot t/q_t versus$t$. Pseudo-second-order kinetic adsorption by $ZnCl_2$-BC for organic matters from TNT red water at 30 – 60 ± 0.2℃ at different temperatures is shown in Fig. 9(a). The higher correlation coefficient value ($R^2 = 1.0000$) listed in Table 4 indicates that the organic matters of TNT red water uptake by $ZnCl_2$-BC follows pseudo-second-order model. The result is accordance with that of organic matters from TNT red water by BC [12].

3.9.3. Intraparticle diffusion models

The intraparticle diffusion equation can be presented as follows [40]:

$$q_t = k_{pi} t^{1/2} + c_i \tag{18}$$

where k_{pi} (mg/g $\text{min}^{1/2}$) and c_i is the intraparticle diffusion rate constant and the intercept at stage i.

The intraparticle diffusion model provides insight to the mechanism and rate-controlling steps that affect the kinetics. Fig. 9(b) shows the pore diffusion plot of organic matter adsorption by the $ZnCl_2$-BC at 30, 40, 50, and 60 ± 0.2℃. If the plot passes through the origin, the plot of q_t vs, $t^{1/2}$ will be linear and then the rate is limited by intraparticle diffusion, otherwise, another mechanism together with intraparticle diffusion is involved. As shown in Fig. 9(b), the adsorption process shows two linear portions over all time. The first sharper portion corresponds to external surface adsorption or instantaneous adsorption and the second portion shows gradual adsorption where intraparticle diffusion is rate limiting [41]. Table 4 lists the corresponding model parameters. At all studied temperatures, k_{p1} is larger than k_{p2}, and c_2 is higher than c_1. This indicates that the adsorption efficiency is higher in the beginning due to the large number of vacant sites on the $ZnCl_2$-BC surface. After the adsorbed matters form a thick layer, the adsorption capacity of $ZnCl_2$-BC is exhausted and the adsorption efficiency is controlled by the rate at which the adsorbent is transported from the exterior to the interior sites of the adsorbent.

3.10. Determination of the activation energy

The pseudo-second-order rate constant is expressed as a function of temperature by the following Arrhenius-type relationship [38]:

$$K_2 = K_0 e^{-E_a/\text{RT}} \tag{19}$$

where k_0 is the temperature independent factor (g/mg min), E is the activation energy of adsorption (J/mol), R is gas constant (8.314 J/mol K), and T is the absolute temperature (K). The activation energy for the adsorption of organic matters from TNT red water was calculated according to Eq. (19) and was found to be 5.82 kJ/mol. In general, activation energy for physical adsorption is smaller; while higher for chemical adsorption [39]. The relative low activation energy for $ZnCl_2$-BC to adsorb organic matters from TNT red water shows the adsorption process is physical process.

3.11. Mechanisms of adsorption

The results of D–R model, adsorption activation energy, and thermodynamic analyses show that the

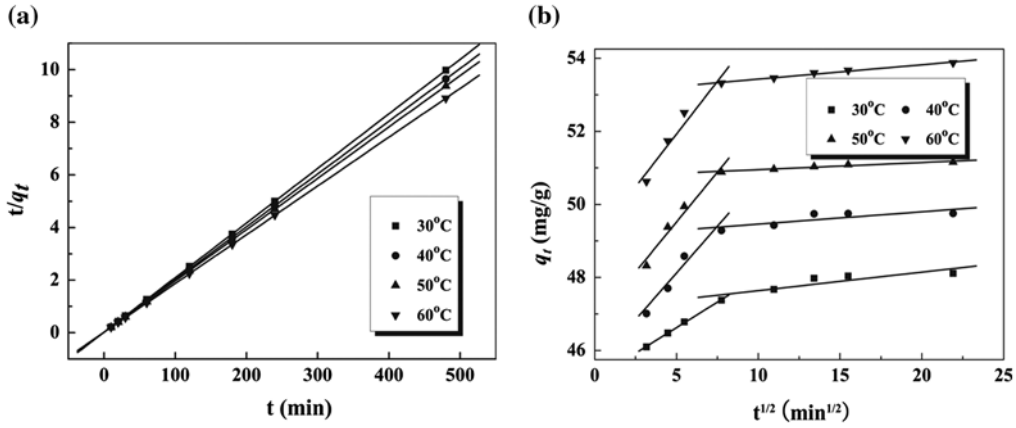

Fig. 9. Pseudo-second-order adsorption kinetics (a), and intraparticle diffusion kinetics (b) for the adsorption of organic matters on $ZnCl_2$-BC (adsorbent dosage = 0.3 g/25 mL, ratio of dilution = 1:100, and contact time = 480 min).

Table 4
Parameters of Pseudo-second-order and intraparticle diffusion models for the adsorption of organic matters from TNT red water on $ZnCl_2$-BC

Kinetic models	Parameters	30℃	40℃	50℃	60℃
Pseudo-second-order model	q_e (cal)(mg/g)	48.19	49.85	51.22	53.94
	k_2 (g/mg min)	0.0247	0.0282	0.0305	0.0289
	R^2	0.9999	0.9999	0.9999	0.9999
Intraparticle diffusion model	K_{ip1} (mg/g $min^{0.5}$)	0.2793	0.5035	0.5459	0.5775
	R_1^2	0.9990	0.9575	0.9697	0.9482
	C_1	45.23	45.52	46.79	49.04
	K_{ip2} (mg/g $min^{0.5}$)	0.0506	0.0338	0.0195	0.0393
	R_2^2	0.7872	0.6741	0.9490	0.9853
	C_2	47.13	49.12	50.76	53.04
	q_e (exp) (mg/g)	47.13	49.12	50.76	53.04

Notes: Adsorbent dosage = 0.3 g/25 mL; Dilution ratio = 1:100; Temperature = 30 – 60 ± 0.2℃ and Contact time = 480 min.

adsorption is a physical process. Therefore, the van der Waals force is involved in the adsorption mechanism. In addition, hydrogen bonding interaction between organic matters and $ZnCl_2$-BC act as a dominant role in adsorption process because the value of ΔH is 11.49 kJ/mol from the thermodynamic analyses. As demonstrated by the results of Boehm's titration (Table 1) and the main adsorption groups of the $ZnCl_2$-BC are carboxylic, phenolic groups, and lactonic groups. The hydrogen atoms of these groups in $ZnCl_2$-BC can form hydrogen bonding with nitrogen and oxygen atoms from the NBCs of TNT red water. On the other hand, the oxygen of the groups in the $ZnCl_2$-BC can also act by hydrogen bonding with hydrogen atoms of −COOH, −OH, HSO_3^-, and $-NH_2$ from the NBCs of TNT red water. The n-π donor–acceptor interaction can also be included between the electron pair of carbonyl O acting as donor and the π-acceptor of aromatic compounds (α-TNT, α-nitrophenols, α-nitrobenzoic acid, and other nitrobenzene compounds). Except these interactions, the adsorption mechanism may be related to the theory proposed by Pearson [13]. Based on Pearson's classification, Zn^{2+} is a borderline acid, Zn^{2+}can enhance the borderline acid of BC. TNT red water belongs to soft base. According to the HSAB theory, borderline acids prefer to bond to soft bases [13,14]. Therefore, the adsorption of organic matter by $ZnCl_2$-BC can be related to the hard and soft acid and base (HSAB) theory.

In summary, the mechanisms of adsorption are related with the van der Waals force, hydrogen bonding formation, electron donor–acceptor interaction, and HSAB theory.

4. Conclusion

$ZnCl_2$-BC is an effective adsorbent for the removal of organic matters from TNT red water. The optimal

conditions for organic matters removal are: adsorbent dosage = 0.3 g/25 mL, pH 2.0, and equilibrium time = 180 min. The equilibrium adsorption data are best fitted by Langmuir isotherm. The adsorption kinetics is found to follow pseudo-second-order model. Thermodynamic analysis indicates that adsorption of organic matters from TNT red water by $ZnCl_2$-BC is an endothermic, spontaneous process, and the randomness at the solid/solution interface increases at studied temperatures. The adsorption of organic matters from TNT red water on $ZnCl_2$-BC is physical process by analyzing D–R isotherm, activation energy, and thermodynamic. The mechanisms of adsorption are related with the van der Waals force, hydrogen bonding formation, electron donor–acceptor interaction, and HSAB theory. The $ZnCl_2$-BC shows excellent adsorption characteristics and can be used in the removal of organic matters from TNT red water.

Acknowledgments

This research was jointly supported by National High Technology Research and Development Program (863 Program 2012AA06A109) of China, the Fundamental Research Funds for the Central Universities (2010ZD08), the special co-construction project of Beijing city education committee, Doctoral Program Foundation of Institution of higher education of China (22-08-07), and City University of Hong Kong Strategic Research Grant (SRG, 7008009).

References

[1] E.K. Nefso, S.E. Burns, C.J. McGrath, Degradation kinetics of TNT in the presence of six mineral surfaces and ferrous iron, J. Hazard. Mater. 123 (2005) 79–88.
[2] Q.L. Zhao, Z.F. Ye, M.H. Zhang, Treatment of 2,4,6-trinitrotoluene (TNT) red water by vacuum distillation, Chemosphere 80 (2010) 947–950.
[3] Z.L. Xiao, S.Q. Hu, X.Q. Wu, J.Y. Wang, The Safety and Environmental Technology of Propellant and Explosive Beijing Institute of Technology University Press, Beijing, 2006, pp. 267–268.
[4] M.H. Zhang, Q.L. Zhao, Z.F. Ye, Organic pollutants removal from 2,4,6-trinitrotoluene (TNT) red water using low cost activated coke, J. Environ Sci. 23 (2011) 1962–1969.
[5] F.Q. An, B.J. Gao, X.Q. Feng, Adsorption performance and mechanism of 2,4,6-trinitrotoluene on a novel adsorption material polyvinylbenzyl acid/SiO_2, Appl. Surf. Sci. 255 (2009) 5031–5035.
[6] W.S. Chen, W.C. Chiang, K.M. Wei, Recovery of nitrotoluenes from wastewater by solvent extraction enhanced with salting-out effect, J. Hazard. Mater. 147 (2007) 197–204.
[7] S. Hwang, E.J. Bouwer, S.L. Larson, J.L. Davis, Decolorization of alkaline TNT hydrolysis effluents using UV/H_2O_2, J. Hazard. Mater. 108 (2004) 61–67.
[8] S.V. Muhammad, T. Keiichi, Photocatalytic degradation of nitrotoluene in aqueous TiO_2 suspension, Water Res. 36 (2002) 59–64.
[9] R. Matta, K. Hanna, T. Kone, Oxidation of 2,4,6-trinitrotoluene in the presence of different iron-bearing minerals at neutral pH, Chem. Eng. J. 144 (2008) 453–458.
[10] S.W. Maloney, N.R. Adrian, R.F. Hickey, Anaerobic treatment of pink water in a fluidized bed reactor containing GAC, J. Hazard Mater. 92 (2002) 77–88.
[11] I. Abe, T. Fukuhara, J. Maruyama, H. Tatsumoto, S. Iwasaki, Preparation of carbonaceous adsorbents for removal of chloroform from drinking water, Carbon 39 (2001) 1069–1073.
[12] D. Fu, Y.H. Zhang, F.Z. Lv, P.K. Chu, J.W. Shang, Removal of organic materials from TNT red water by bamboo charcoal adsorption, Chem. Eng. J. 193–194 (2012) 39–49.
[13] R.G. Pearson, Hard and soft acids and bases, J. Am. Chem. Soc. 85 (1963) 3533–3539.
[14] F.F. Wei, Y.H. Zhang, F.Z. Lv, P.K. Chu, Z.F. Ye, Extraction of organic materials from red water by metal-impregnated lignite activated carbon, J. Hazard. Mater. 197 (2011) 352–360.
[15] K. Mizuta, T. Matsumoto, Y. Hatate, K. Nishihara, T. Nakanish, Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal, Bioresource Technol. 95 (2004) 255–257.
[16] A.M.M. Vargas, A.L. Cazetta, M.H. Kunita, T.L. Silva, V.C. Almeida, Adsorption of methylene blue on activated carbon produced from flamboyant pods (Delonix regia): Study of adsorption isotherms and kinetic models, Chem. Eng. J. 168 (2011) 722–730.
[17] W.P. Liu, J.P. Zhou, K.Q. Qiu, S.W. Xiao, Surface modification and characterization of zinc oxide whiskers, China Plast. Ind. 5 (2004) 49–51.
[18] A. Özer, G. Akkaya, M. Turabik, Biosorption of acid blue 290 (AB 290) and acid blue 324 (AB 324) dyes on Spirogyra rhizopus, J. Hazard. Mater. 135 (2006) 355–364.
[19] J.P. Zhang, X.Y. Lin, X.G. Luo, C. Zhang, H. Zhu, A modified lignin adsorbent for the removal of 2,4,6-trinitrotoluene, Chem. Eng. J. 168 (2011) 1055–1063.
[20] S.R. Kyoung, A. Venugopal, D.D. Adrian, D. Constant, K. Qaisi, K.T. Valsaraj, L.J. Thibodeaux, D. Roy, Solubility of 2,4,6-Trinitrotoluene (TNT) in Water, J. Chem. Eng. Data 41 (1996) 758–761.
[21] F.Y. Wang, H. Wang, J.W. Ma, Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent-bamboo charcoal, J. Hazard. Mater. 177 (2010) 300–306.
[22] C.V. Srivastava, M.M. Swamy, D.I. Mall, P. Basheswar, M.I. Mishra, Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics, Colloids Surf. A: Physicochem. Eng. Aspects. 272 (2006) 89–104.
[23] N. Nasuha, B.H. Hameed, T. Azam, M. Din, Rejected tea as a potential low-cost adsorbent for the removal of methylene blue, J. Hazard. Mater. 175 (2010) 126–132.
[24] S. Karagoz, T. Tay, S. Ucar, M. Erdem, Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption, Bioresource Technol. 99 (2008) 6214–6222.

[25] Y.J. Yao, F.F. Xu, M. Chen, Z.X. Xu, Z. Zhu, Adsorption behavior of methylene blue on carbon nanotubes, Bioresource Technol. 101 (2010) 3040–3046.
[26] K. Saltali, A. Sari, M. Aydin, Removal of ammonium ion from aqueous solution by natural Turkish zeolite for environmental quality, J. Hazard. Mater. 141 (2007) 258–263.
[27] H. Zheng, Y. Wang, Y. Zheng, H. Zhang, S. Liang, M. Long, Equilibrium, kinetic and thermodynamic studies on the sorption of 4-hydroxyphenol on Cr-bentonite, Chem. Eng. J. 143 (2008) 117–123.
[28] H.M.F. Freundlich, Über die adsorption in lösungen [About the adsorption in solution], Zeitschrift fur Physikalische Chemie [J. Phys. Chem. A.] (Leipzig). 57 (1906) 385–470.
[29] K.K.H. Choy, G. McKay, J.F. Porter, Sorption of acid dyes from effluents using activated carbon, Resour. Conserv. Recy. 27 (1999) 57–71.
[30] D.H. Reddy, K. Seshaiah, A.V.R. Reddy, M.M. Rao, M.C. Wang, Biosorption of Pb^{2+} from aqueous solutions by Moringa oleifera bark: Equilibrium and kinetic studies, J. Hazard. Mater. 174 (2010) 831–838.
[31] Z. Aksu, Determination of equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nikel (II) ions onto Chlorella vulgaris, Process Biochem. 38 (2002) 89–99.
[32] P. Lodeiro, J.L. Barriada, R. Herrero, The marine macroalga Cystoseira baccata as biosorbent for cadmium (II) and lead (II) removal Kinetic and equilibrium studies, Environ. Pollut. 142 (2006) 264–273.
[33] B. Kannamba, K. Laxma Reddy, B.V. AppaRao, Removal of Cu (II) from aqueous solutions using chemically modified chitosan, J. Hazard. Mater. 175 (2010) 939–948.
[34] A. Kumar, B. Prasad, I.M. Mishra, Adsorptive removal of acrylonitrile by commercial grade activated carbon: Kinetics, equilibrium and thermodynamics, J. Hazard. Mater. 152 (2008) 589–600.
[35] V.B. Oepen, W.K. Ordel, W. Klein, Sorption of nonpolar and polar compounds to soils: Processes, measurements and experience with the applicability of the modified OECD-Guideline 106, Chemosphere 22 (1991) 285–304.
[36] H. Zheng, L.J. Han, H.W. Ma, Y. Zheng, H.M. Zhang, D.H. Liu, S. Liang, Adsorption characteristics of ammonium ion by zeolite 13X, J. Hazard. Mater. 158 (2008) 577–584.
[37] K.K. Panday, G. Prasad, V.N. Singh, Use of wollastonite for the treatment of Cu (II) rich effluents, Water Air Soil Pollut. 27 (1986) 287–296.
[38] A. Özer, G. Akkaya, M. Turabik, The biosorption of Acid Red 337 and Acid Blue 324 on Enteromorpha prolifera: The application of nonlinear regression analysis to dye biosorption, Chem. Eng. J. 112 (2005) 181–190.
[39] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.
[40] W.J. Weber Jr, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. 89 (1963) 31–59.
[41] F.C. Wu, R.L. Tseng, R.S. Juang, Comparisons of porous and adsorption properties of carbons activated by steam and KOH, J. Colloid Interf. Sci. 283 (2005) 49–56.